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(21) International Application Number: PCT/US98/00316 (22) International Filing Date: 12 January 1998 (12.01.98) (30) Priority Data: 60/034,933 13 January 1997 (13.01.97) US (71) Applicants (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF NORTH CAROLINA-CHAPEL HILL [US/US]; Office of Technology Development, Campus Box 4105, 308 Bynum Hall, Chapel Hill, NC 27599-4105 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BROOKHART, Maurice, S. [US/US]; 944 Old Lystra Road, Chapel Hill, NC 27514 (US). SMALL, Brooke, L. [US/US]; 4-A Royal Park, 501 Highway 54 Bypass, Carrboro, NC 27510 (US). (74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, GW, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERIZATION OF PROPYLENE (57) Abstract <p>Propylene may be polymerized by contacting it with certain iron complexes of selected 2,6-pyridinecarboxaldehydebis (imines) and 2,6-diacetylpyridinebis (imines). The polymers produced are useful as molding resins.</p>		

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TITLE
POLYMERIZATION OF PROPYLENE

This application claims the benefit of U.S.
5 Provisional Application No. 60/034,933, filed
January 13, 1997.

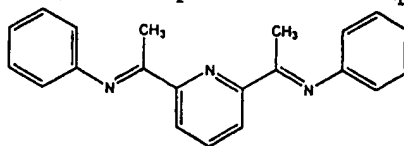
FIELD OF THE INVENTION

Selected iron complexes of
10 2,6-pyridinecarboxaldehydebis(imines) and
2,6-diacetylpyridinebis(imines) are catalysts for the
polymerization of propylene.

FIELD OF THE INVENTION

Polymers of propylene are important items of
15 commerce, millions of tons being produced annually.
These polymers are used in a myriad of ways, for
instance being used for fibers, films, molding resins,
etc. In most cases, propylene is polymerized using a
catalyst, often a transition metal compound or complex.
20 These catalysts vary in cost per unit weight of
polypropylene produced, the structure of the polymer
produced, the possible need to remove the catalyst from
the polypropylene, the toxicity of the catalyst, etc.
Due to the commercial importance of polypropylenes, new
25 polymerization catalysts are constantly being sought.

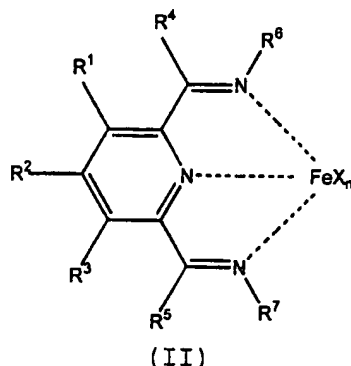
P. E. Figgins, et al., J. Am. Chem. Soc., vol. 82,
p. 820-824, and/or F. Lions, et al., J. Am. Chem. Soc.,
vol. 79, p. 2733-2738 report the synthesis of certain
2,6-diacetylpyridinebis(imines) and certain iron
30 complexes of these tridentate ligands. Japanese Patent
Application 02-078,663 reports the compound



and an iron[II] complex of this latter compound in
which two molecules of the 2,6-
35 diacetylpyridinebis(imine) are present in the complex.
None of these references reports that these compounds
polymerize propylene.

SUMMARY OF THE INVENTION

This invention concerns a first process for the polymerization of propylene, comprising, contacting, at a temperature of about -40°C to about $+300^{\circ}\text{C}$, a
 5 compound of the formula



with propylene and:

(a) a first compound W, which is a neutral
 10 Lewis acid capable of abstracting X^- , an alkyl group or a hydride group from M to form WX^- , $(\text{WR}^{20})^-$ or WH^- and which is also capable of transferring an alkyl group or a hydride to M, provided that WX^- is a weakly coordinating anion; or

15 (b) a combination of second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^- , a hydride or an alkyl group from M to form a weakly coordinating anion;

20 wherein:

each X is an anion;

n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe atom present in (II);

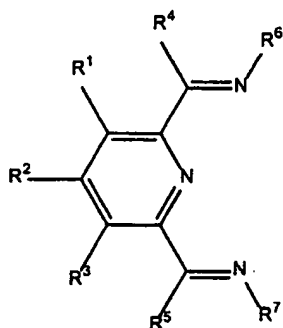
25 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted

30 hydrocarbyl;

R^6 and R^7 are aryl or substituted aryl; and R^{20} is alkyl.

This invention also concerns a second process for the polymerization of propylene, comprising contacting, at a temperature of about -40°C to about $+300^{\circ}\text{C}$, a Fe[II] or Fe[III] complex of a tridentate ligand of the
 5 formula



(I)

with propylene, wherein:

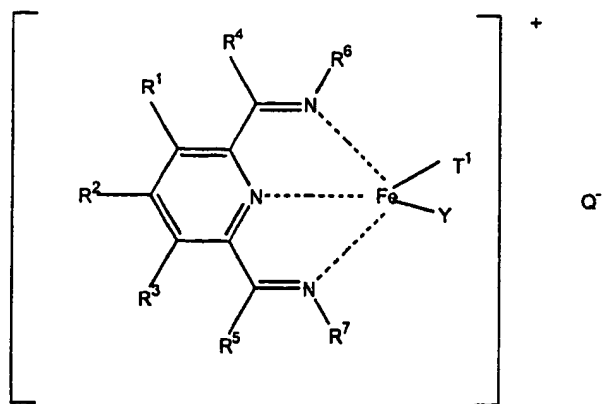
R¹, R² and R³ are each independently hydrogen,
 10 hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

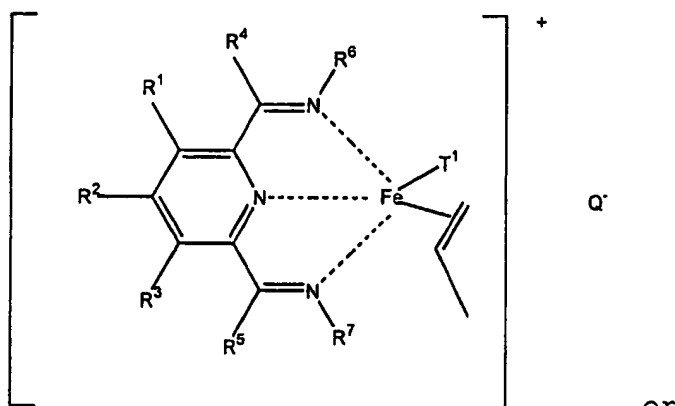
15 R⁶ and R⁷ are aryl or substituted aryl;

and provided that an Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said propylene, and a ligand that may add to said propylene.

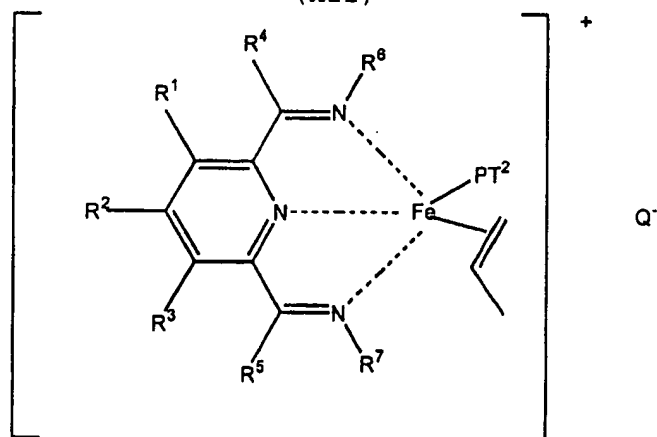
20 This invention also concerns a third process for the polymerization of propylene, comprising, contacting, at a temperature of about -40°C to about $+300^{\circ}\text{C}$, propylene and a compound of the formula



(VII)



(XII)



(IX)

wherein:

R^1 , R^2 and R^3 are each independently hydrogen,
 10 hydrocarbyl, substituted hydrocarbyl, or an inert
 functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

5 T^1 is hydride or alkyl or any other anionic ligand into which propylene can insert;

Y is a vacant coordination site or a neutral ligand capable of being displaced by propylene;

Q is a relatively non-coordinating anion;

10 P is a divalent polymeric group; and

T^2 is an end group.

DETAILS OF THE INVENTION

Herein, certain terms are used. Some of them are:

o A "hydrocarbyl group" is a univalent group
15 containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

o By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more
20 substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted
25 hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.

o By "(inert) functional group" herein is meant a group other than hydrocarbyl or substituted
30 hydrocarbyl which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially interfere with any process described herein that the compound in which they are present may
35 take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), ether such as -OR¹⁸ wherein R^{18} is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near an iron atom, such as R^4 , R^5 , R^8 , R^{12} , R^{13} ,
40 and R^{17} the functional group should not coordinate to the metal atom more strongly than the groups in

compounds containing R^4 , R^5 , R^8 , R^{12} , R^{13} , and R^{17} (see below for definitions of these groups) which are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

5 ◦ By an "alkyl aluminum compound" is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide, hydride, and halogen may also be bound to aluminum atoms in the compound.

10 ◦ By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base. Examples of such compounds include ethers, amines, sulfides, and organic nitriles.

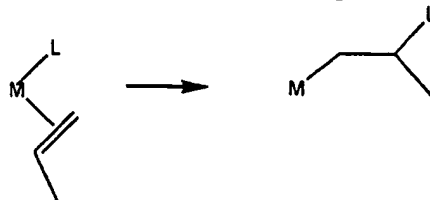
 ◦ By "cationic Lewis acid" is meant a cation
15 which can act as a Lewis acid. Examples of such cations are sodium and silver cations.

 ◦ By relatively noncoordinating (or weakly coordinating) anions are meant those anions as are generally referred to in the art in this manner, and
20 the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by
25 reference. Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X^- , including $R^{19}_3AlX^-$, $R^{19}_2AlClX^-$, $R^{19}AlCl_2X^-$, and " $R^{19}AlOX^-$ ", wherein R^{19} is alkyl containing 1 to 25 carbon atoms. Other useful
30 noncoordinating anions include BAF^- (BAF^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), SbF_6^- , PF_6^- , and BF_4^- , trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N^-$, and $(C_6F_5)_4B^-$.

 ◦ By an empty coordination site is meant a
35 potential coordination site that does not have a ligand bound to it. Thus if a propylene molecule is in the proximity of the empty coordination site, the propylene molecule may coordinate to the iron atom.

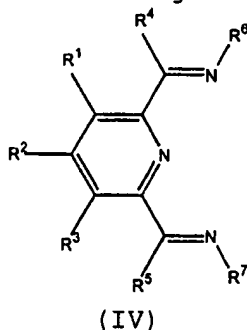
 ◦ By a ligand that may add to propylene is
40 meant a ligand coordinated to an iron atom into which a propylene molecule (or a coordinated propylene

molecule) may insert to start or continue a polymerization. For instance, this may take the form of the reaction (wherein L is a ligand):



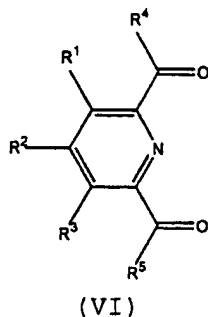
- 5 Note the similarity of the structure on the left-hand side of this equation to compound (IX) (see below).

Compounds useful as ligands herein in iron complexes are diimines of 2,6-pyridinedicarboxaldehyde or 2,6-diacylpyridines of the general formula



- 10 wherein R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group, R^4 and R^5 are each independently
 15 hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl, and R^6 and R^7 are aryl or substituted aryl.

(IV) may be made by the reaction of a compound of the formula



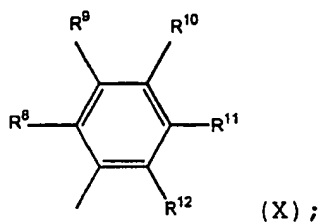
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with a compound of the formula H_2NR^6 or H_2NR^7 , wherein R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert

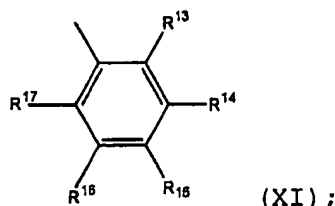
functional group, R^4 and R^5 are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, R^4 and R^5 are each hydrocarbyl or substituted hydrocarbyl, and R^6 and R^7 are aryl or substituted aryl. These
 5 reactions are often catalyzed by carboxylic acids, such as formic acid. Reactions such as these are described in Experiments 1-4.

In (III), and hence in (I), (II), (IV), (VII), (IX) and (XII) that match the formula of (III), it is
 10 preferred that:

R^6 is



R^7 is



R^8 and R^{13} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;
 R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;
 20 R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are vicinal to one
 25 another, taken together may form a ring.

Preferred compounds of formula (IV) and compounds in which (IV) is a ligand are those of compound (III) [note that (III) is a subset of (IV)], whether present in compounds such as (I), (II), (IV), (VI), (IX) and
 30 (XII). In (III), and hence in (I), (II), (IV), (VI), (IX) and (XII) that match the formula of (III), it is preferred that:

R^1 , R^2 and R^3 are hydrogen; and/or
 R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} is each
independently halogen, alkyl containing 1 to 6 carbon
atoms, or hydrogen, and it is more preferred that each
5 of these is hydrogen; and/or

R^8 and R^{13} is each independently hydrogen,
halogen, or alkyl containing 1 to 6 carbon atoms, and
it is especially preferred that each R^8 and R^{13} is alkyl
containing 1-6 carbon atoms, and it is more preferred
10 that R^8 and R^{13} are methyl, i-propyl or t-butyl (but
both R^8 and R^{12} or both R^{13} and R^{17} can't be t-butyl in
the same compound);

R^{12} and R^{17} is each independently halogen,
hydrogen, or alkyl containing 1 to 6 carbon atoms, and
15 it is it especially preferred that each R^{12} and R^{17} is
alkyl containing 1-6 carbon atoms, and it is more
preferred that R^{12} and R^{17} are methyl or i-propyl;

R^4 and R^5 are each independently halogen,
hydrogen or alkyl containing 1 to 6 carbon atoms, and
20 it is especially preferred that R^4 and R^5 are each
independently hydrogen or methyl.

Specific preferred compounds (III) [and also in
(I), (II), (IV), (VI), (IX) and (XII)] are:

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are
25 hydrogen, R^4 and R^5 are methyl, and R^8 , R^{12} , R^{13} and R^{17}
are isopropyl;

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are
hydrogen, R^4 and R^5 are methyl, and R^8 , R^{12} , R^{13} and R^{17}
are methyl;

30 R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{12} , R^{14} , R^{15} , R^{16} and
 R^{17} are hydrogen, R^4 and R^5 are methyl, and R^8 , and R^{13}
are t-butyl; or

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} , R^{16} , R^8 , R^{12} ,
 R^{13} and R^{17} are hydrogen, and R^4 and R^5 are methyl.

35 In the polymerization processes described herein,
it can be seen from the results that it is preferred
that there be at least some steric crowding caused by
the tridentate ligand about the Fe atom. Therefore, it
is preferred that groups close to the metal atom be
40 relatively large. It is relatively simple to control
steric crowding if (III) is the tridentate ligand,

since control of steric crowding can be achieved simply by controlling the size of R^8 , R^{12} , R^{13} and R^{16} . These groups may also be part of fused ring systems, such as 9-anthracenyl.

5 In the first polymerization process it is preferred that X is chloride, bromide or nitrate.

In the first polymerization process described herein an iron complex (II) is contacted with propylene and a neutral Lewis acid W capable of abstracting X^- ,
10 hydride or alkyl from (II) to form a weakly coordinating anion, and must alkylate or be capable of adding a hydride ion to the metal atom, or an additional alkylating agent or an agent capable of adding a hydride anion to the metal atom must be
15 present. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF_5 , Ar_3B (wherein Ar is aryl), and BF_3 . Suitable cationic Lewis acids or Bronsted acids include NaBAF, silver trifluoromethanesulfonate, HBf_4 , or
20 $[C_6H_5NH(CH_3)_2]^+[B(C_6F_5)_4]^-$. In those instances in which (II) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal atom, the neutral Lewis
25 acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal or a separate alkylating or hydriding agent is present, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

30 It is preferred that R^{20} contains 1 to 4 carbon atoms, and more preferred that R^{20} is methyl or ethyl.

For instance, alkyl aluminum compounds (see next paragraph) may alkylate (II). However, not all alkyl aluminum compounds may be strong enough Lewis acids to
35 abstract X^- or an alkyl group from the metal atom. In that case a separate Lewis acid strong enough to do the abstraction must be present. For instance, polymethylaluminoxane may be used as the "sole" Lewis acid, it both alkylates and does the abstraction from
40 the metal atom. Triethylaluminum, however, alkylates the metal atom, but may not be a strong enough Lewis

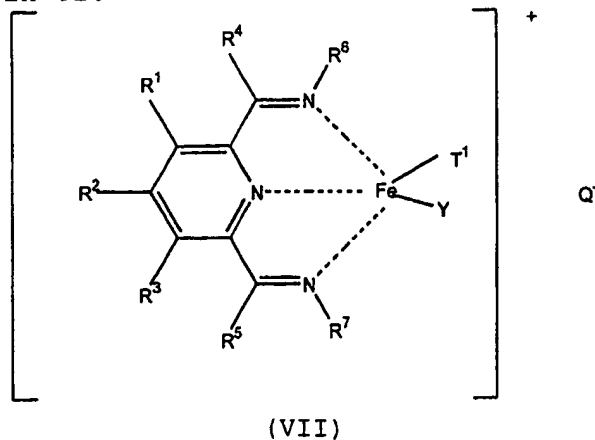
acid to abstract an anion from the metal atom, so another (stronger) Lewis acid, $B(C_6F_5)_3$, may also be added to the polymerization. Without the stronger Lewis acid, $B(C_6F_5)_3$, present, the polymerization may not proceed.

A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as R^{19}_3Al , $R^{19}AlCl_2$, R^{19}_2AlCl , and " $R^{19}AlO$ " (alkylaluminoxanes), wherein R^{19} is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula $[MeAlO]_n$), $(C_2H_5)_2AlCl$, $C_2H_5AlCl_2$, and $[(CH_3)_2CHCH_2]_3Al$.

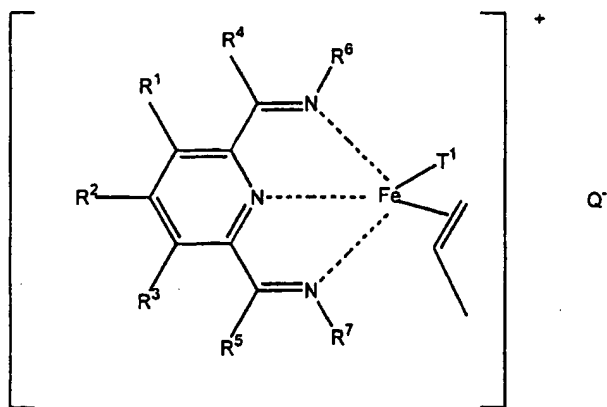
Metal hydrides such as $NaBH_4$ may be used to bond hydride groups to the metal M.

In the second polymerization process described herein an iron complex of (I) is either added to the polymerization process or formed in situ in the process. In fact, more than one such complex may be formed during the course of the process, for instance formation of an initial complex and then reaction of that complex to form a living ended polymer containing such a complex.

Examples of such complexes which may be formed initially in situ include



and



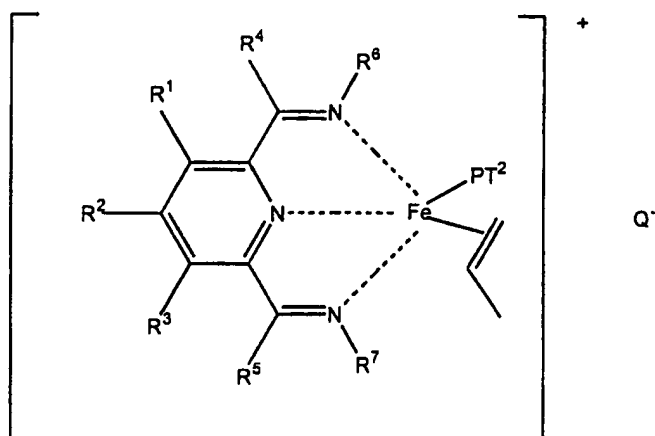
(XII)

wherein R^1 through R^7 are as defined above, T^1 is
 5 hydride or alkyl or any other anionic ligand into which
 propylene can insert, Y is a neutral ligand capable of
 being displaced by propylene or a vacant coordination
 site, the structure



10 represents a propylene molecule coordinated to the Fe,
 and Q is a relatively non-coordinating anion.
 Complexes may be added directly to the process or
 formed in situ. For instance, (VII) may be formed by
 the reaction of (II) with a neutral Lewis acid such as
 15 an alkyl aluminum compound. Another method of forming
 such a complex in situ is adding a suitable iron
 compound such as iron chloride compound, (I) and an
 alkyl aluminum compound. Other iron salts in which
 anions similar to chloride are present, and which may
 20 be removed by reaction with the Lewis or Bronsted acid
 may be employed. For instance metal halides, nitrates
 and carboxylates (such as acetates) may be used,
 particularly if they are slightly soluble in the
 process medium. It is preferred that these precursor
 25 metal salts be at least somewhat soluble in the process
 medium.

After the propylene polymerization has started,
 the complex may be in a form such as



(IX)

wherein R^1 through R^7 , and Q are as defined above, and P is a divalent polypropylene group, and T^2 is an end group, for example the groups listed for T^1 above. T^2 may be any group such as T^1 which is capable of being coordinated to the iron atom, and also capable of "adding" to a propylene molecule. It is preferred that the Fe atom be in +2 oxidation state in (VII), (VIII) and (IX). Compounds such as (VII), (IX) and (XII) may or may not be stable away from an environment similar to that of the polymerization process.

(VII), (IX) and (XII) may also be used, in the absence of any "co-catalysts" or "activators" to polymerize propylene in a third polymerization process. Except for the ingredients in the process, the process conditions for the third process, such as temperature pressure, polymerization medium, etc., may be the same as for the first and second polymerization processes, and preferred conditions for those processes are also preferred for the third polymerization process.

In all the polymerization processes herein, the temperature at which the propylene polymerization is carried out is about -40°C to about $+300^\circ\text{C}$, preferably about -25°C to about 150°C , more preferably about 0°C to about 100°C . The propylene pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa, preferably about atmospheric pressure and 5 MPa, being a suitable range.

The polymerization processes herein may be run in the presence of various liquids, particularly aprotic

organic liquids. The catalyst system, propylene, and polypropylene may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids
5 include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

The propylene polymerizations herein may also initially be carried out in the solid state [assuming
10 (II), (III) (IV) or (VII) is a solid] by, for instance, supporting (II), (III) (IV) or (VII) on a substrate such as silica or alumina, activating it with the Lewis (such as W, for instance an alkylaluminum compound) or Bronsted acid and exposing it to propylene. The
15 support may also be able to take the place of the Lewis or Bronsted acid, for instance an acidic clay such as montmorillonite. Another method of making a supported catalyst is to start a polymerization or at least make an iron complex of another olefin or oligomer of an
20 olefin such as cyclopentene on a support such as silica or alumina. These "heterogeneous" catalysts may be used to catalyze polymerization in the gas phase or the liquid phase. By gas phase is meant that the propylene is transported to contact with the catalyst particle
25 while the propylene is in the gas phase.

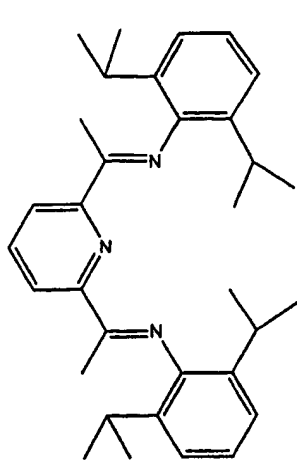
In all of the polymerization processes described herein oligomers and polymers of propylene are made. They may range in molecular weight from oligomeric olefins, to lower molecular weight polypropylene waxes
30 and liquids, to higher molecular weight polypropylene.

In the Examples and Experiments, the following abbreviations and terms are used:

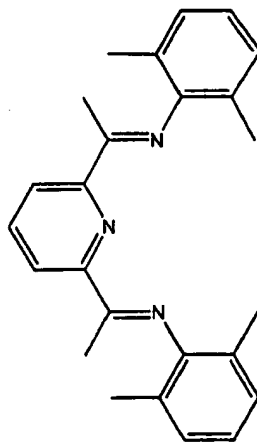
MeOH - methanol
35 Mn - number average molecular weight
Mw - weight average molecular weight
MMAO - polymethylaluminoxane purchased from Akzo, Inc. as a 7 weight percent solution in toluene.

In the Experiments and Examples the following
40 compounds are made and/or used. Compounds (XXI) and

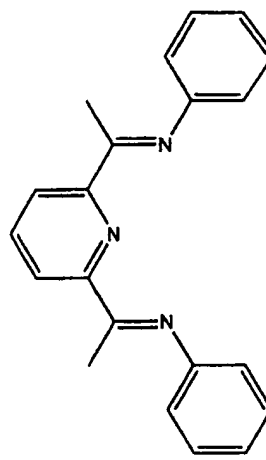
(XXII) were made by methods similar to those for (XVII) - (XX).



(XIII)

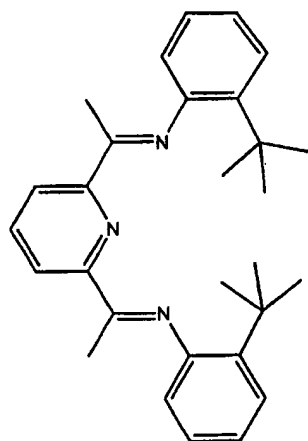


(XIV)

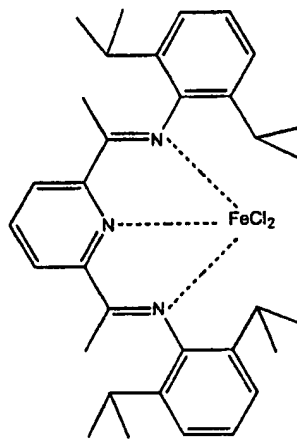


(XV)

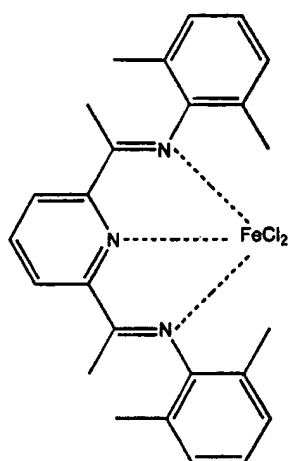
5



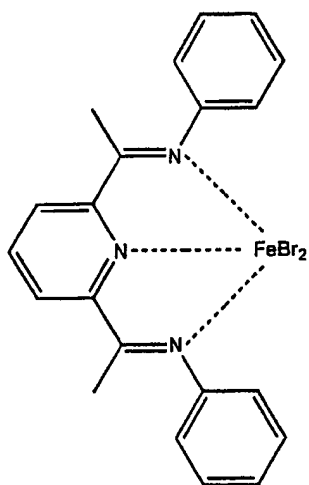
(XVI)



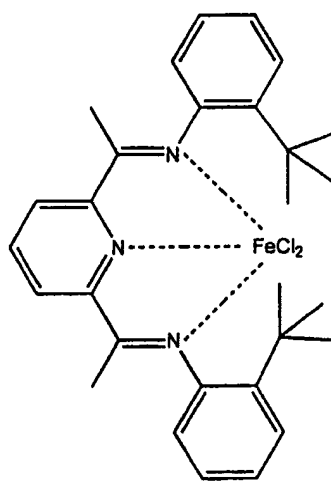
(XVII)



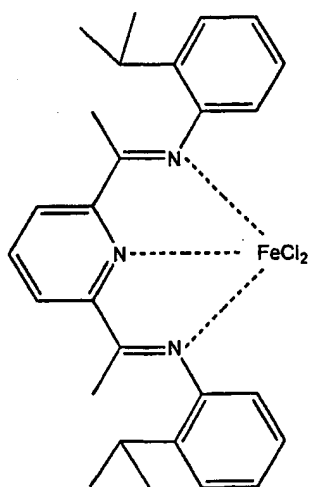
(XVIII)



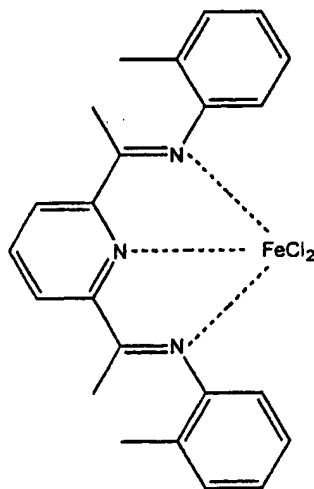
(XIX)



(XX)



(XXI)



(XXII)

Experiment 1

2,6-Diacetylpyridine (250 mg) was weighed into a 50 ml Schlenk flask, 50 ml of MeOH was added and stirring was started with a magnetic stirring bar. Then 2.5 ml (5 eq.) of 2,6-diisopropylaniline was added via syringe followed by 3 drops of formic acid. The mixture was allowed to stir for 3 days, after which time 260 mg of a light yellow solid was collected by filtration and washed with MeOH. Successive crops of solid were collected giving a total yield of 520 mg (70.5%) of (XIII). ¹H NMR (CDCl₃): 1.15 (d, 24H), 2.25(s, 6H), 2.80 (septet, 4H), 7.15(m, 6H), 7.90(t, 4H), 8.45(d, 2H).

Experiment 2

2,6-Diacetylpyridine (1.0 g) was weighed into a 100 ml flask, 50 ml of MeOH was added and stirring was started with a magnetic stirring bar. Then 8.0 ml (10.58 eq.) of 2,6-dimethylaniline was added followed by 5 drops of formic acid. The mixture was allowed to stir overnight. Since no solid had formed, the reaction was heated overnight (second night) at 50°C. The flask was cooled in a wet ice bath and a yellow solid formed and was collected by filtration and washed with cold MeOH. A second crop of solid was collected giving a total yield of 1.29 g (57.1%) of (XIV). ¹H NMR (CDCl₃): 2.05(s, 12H), 2.25(s, 6H), 6.95(t, 2H), 7.05(d, 4H), 7.90(t, 4H), 8.50(d, 2H).

Experiment 3

2,6-Diacetylpyridine (1.0 g) was weighed into a 100 ml flask, 50 ml of MeOH was added and stirring was started with a magnetic stirring bar. Then 8.0 ml (14.4 eq.) of aniline was added followed by 5 drops of formic acid. The mixture was allowed to stir overnight, and a yellow solid formed and was collected by filtration and washed with MeOH. Yield 1.58 g (82.3%) of 95% pure (XV). ¹H NMR (CDCl₃): 2.40(s, 6H), 6.85(d, 4H), 7.12(t, 2H), 7.38(t, 4H), 7.87 (t, 4H), 8.35(d, 2H).

Experiment 4

2,6-Diacetylpyridine (1.0 g) was weighed into a flask, 10 ml of MeOH was added and stirring was started with a magnetic stirring bar. Then 2.5 ml (2.6 eq.) of 2-t-butylaniline was added followed by 5 drops of formic acid. A yellow solid formed within one h, but was indicated to be impure by NMR. Second and third crops were collected under more dilute conditions, yielding a total of 660 mg (25.3%) of pure (XVI). ¹H NMR (CDCl₃): 1.35(s, 18H), 2.40(s, 6H), 6.55(dd, 2H), 7.07(td, 2H), 7.17(td, 2H), 7.42(dd, 2H), 7.93(t, 4H), 8.43(d, 2H pyridyl).

Experiment 5

(XIII) (250 mg, 1.09 eq.) and 95 mg of FeCl₂·4H₂O was weighed into a 10 ml Schlenk flask containing a stirbar. The flask was placed on a Schlenk manifold, backfilled 3 times with argon, and 10 ml of THF were added while stirring. After 2 h, the THF was removed under vacuum. The resulting deep blue solid, (XVII), was washed twice with ether and dried under vacuum.

Experiment 6

(XIV) (200 mg, 1.1 eq.) and 98 mg of FeCl₂·4H₂O was weighed out into a 10 ml Schlenk flask containing a stirbar. The flask was placed on a Schlenk manifold, backfilled 3 times with argon, and 10 ml of THF were added while stirring. After 2 h, the THF was removed under vacuum. The resulting purple solid, (XVIII), was washed twice with ether and dried under vacuum. Elemental analysis: Calc. C, 60.51%; H, 5.48%; N, 8.47%. Found: C, 60.85%; H, 5.95%; N, 6.34%.

Experiment 7

(XV) (200 mg, 1.1 eq.) and 144 mg of FeBr₂·H₂O (13.1% H₂O by weight) was weighed out into a 10 ml Schlenk flask containing a stirbar. The flask was placed on a Schlenk manifold, backfilled 2 times with argon, and 10 ml of THF were added while stirring. After 1 h, the THF was removed under vacuum. The resulting dark purple solid, (XIX), was washed twice with ether and dried under vacuum.

Experiment 8

(XVI) (200 mg, 1.1 eq.) and 84.3 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was weighed out into a 10 ml Schlenk flask containing a stirbar. The flask was placed on a Schlenk manifold, backfilled 3 times with argon, and 10 ml of THF were added while stirring. After 1.5 h, the THF was removed under vacuum. The resulting blue solid, (XX), was washed twice with pentane and dried under vacuum.

Examples 1-15

General Procedure: A 200-300 ml Schlenk flask was fitted with a stopcock and a stirbar, and a septum was used to seal the flask. The flask was then attached to a Schlenk manifold which allowed the flask to be put under vacuum or filled with a gas. The flask was flame dried under vacuum. Propylene was added as a gas and the pressure kept constant at atmospheric pressure. The metal complex was then weighed out to the nearest 0.1 mg, the septum removed and the complex quickly added under a positive gas pressure, and the septum replaced. The flask was then successively evacuated and filled with gas at least 2 times, then was charged by syringe with an organic liquid. The stirring was started and an alkyl aluminum compound (in solution) was added via syringe. If the monomer was not gaseous, the flask was removed from the Schlenk manifold and the polymerization conducted under static Ar pressure. After a given period of time the polymerization was quenched, typically with 6M HCl, and the polymer was precipitated with acetone or methanol. The polymer was filtered off and dried overnight in a vacuum oven. If the acetone or methanol failed to precipitate any polymer, the solvents mixture were allowed to evaporate to isolate any soluble polymers or oligomers.

Table 1 shows the exact conditions for each Example and the results obtained. The "TOF" is the number of moles of propylene polymerized per mole of iron compound used per hour. The M(olecular) W(eight) data is based on Gel Permeation Chromatography results using a toluene solvent and a polystyrene standard. Unless otherwise stated in the "NMR" column, ^1H NMR

were run on all products, and the results indicated that polypropylenes were obtained.

Table 1

Ex. No.	Iron Complex, mg	ml MAO	T(°C)	Rxn Time (h)	Isolated Yield (g)	TOF (x 10 ³ /hr)	MW data	NMR
1	(XVII) 6.0	2.0	0	2.5	1.15	1.1	M _n = 7642, M _w = 10659	¹³ C: regioregular, ~40% mmmm; ¹ H
2	(XVIII) 4.8	2.0	25	5.5	-	-		
3	(XVII) 5.6	2.0	25	5.5	-	-		
4	(XVII) 4.8	2.0	0	3.0	1.2	1.2		¹³ C: regioregular, ~40% mmmm; ¹ H: end groups detectable
5	(XVIII) 4.8	2.0	0	8.0	5.1	1.6		¹³ C: slight weighting toward mmmm; ¹ H: end groups detectable
6	(XX)	2.0	0	1.5	0.2	0.3		¹³ C: regioregular, pentane-soluble fraction ~40% mmmm
7	(XVIII) 4.8	1.2	-5	22.0	13.0	1.5	M _n = 5318, M _w = 9071	¹³ C: regioregular, pentane-soluble fraction ~40% mmmm
8	(XVIII) 9.2	1.2	0	2.0	2.39(2.08 pentane soluble)	1.5		¹³ C(pent sol): ~35% mmmm; ¹ H: end groups detectable, mostly α-olefin
9	(XVIII) 9.3	1.2	-20	2.0	1.78(1.43 pentane soluble)	1.1		¹³ C(pent sol): ~35% mmmm; ¹³ C(pent ins): ~75% mmmm; ¹ H(pent sol): end groups detectable, mostly α-olefin
10	(XVIII) 9.7	1.2	-40	2.0	1.39(0.88 pentane soluble)	0.8		¹³ C(pent sol): ~35% mmmm; ¹³ C(pent ins): ~75% mmmm; ¹ H(pent sol): end groups detectable, mostly α-olefin
11	(XXI) 9.9	1.2	-40	2.0	0.3	-	~C 35 by NMR end group anal.	¹³ C: messy; ¹ H: ~50% internal olefin, small vinylidene peak
12	(XXII) 9.1	1.2	0	2.0	3.3	2.0	~C 35 by NMR end group anal.	¹³ C: messy; ¹ H: ~50% internal olefin, ~15% vinylidene
13	(XXII) 9.1	1.2	-20	2.0	1.4	0.9	~C 35 by NMR end group anal.	¹³ C: messy; ¹ H: ~50% internal olefin, ~15% vinylidene
14	(XXII) 10.5	1.2	-40	2.0	0.9	0.5	~C 35 by NMR end group anal.	¹ H: ~50% internal olefin, ~25% vinylidene
15	(XVII)	1.0	-20	1.5	7.4	9.6	M _n = 8631, M _w = 14391	¹³ C: regioregular, ~70% mmmm

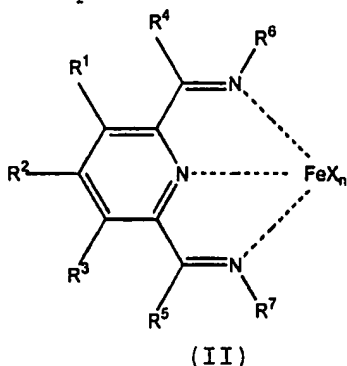
Experiment 9

Using the general procedure of Examples 1-15, 4.4 mg of (XIX), 10 ml of 1-hexene was polymerized at 25°C in 50 ml of toluene, using 1.5 ml of MMAO in toluene as
5 the alkyl aluminum compound. After 24 h the polymerization was quenched, and 1.54 g of an apparently dimeric species was isolated.

CLAIMS

What is claimed is:

1. A process for the polymerization of propylene, comprising, contacting, at a temperature of about -40°C to about $+300^{\circ}\text{C}$, a compound of the formula



with propylene and:

- (a) a first compound W, which is a neutral Lewis acid capable of abstracting X^- and alkyl group or a hydride group from M to form WX^- , WR^{20} or WH and which is also capable of transferring an alkyl group or a hydride to Fe, provided that WX^- is a weakly coordinating anion; or
- (b) a combination of a second compound which is capable of transferring an alkyl or hydride group to M and a third compound which is a neutral Lewis acid which is capable of abstracting X^- , a hydride or an alkyl group from Fe to form a weakly coordinating anion;

wherein:

each X is an anion;

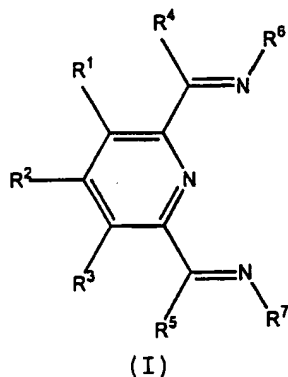
- n is 1, 2 or 3 so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe atom present in (II);

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

- R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group, or substituted hydrocarbyl;

R^6 and R^7 are aryl or substituted aryl; and R^{20} is alkyl.

2. A process for the polymerization of propylene, comprising contacting, at a temperature of about -40°C to about $+300^{\circ}\text{C}$, a Fe[II] or Fe[III] complex of a tridentate ligand of the formula



with propylene, wherein:

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

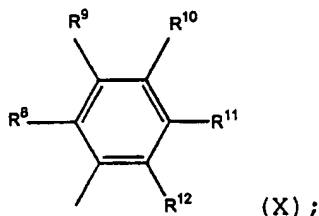
R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

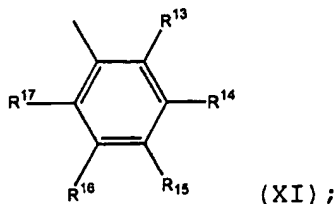
and provided that a Fe[II] or Fe[III] atom also has bonded to it an empty coordination site or a ligand that may be displaced by said propylene and a ligand that may add to said propylene.

3. The process as recited in claim 1 or 2 wherein:

R^6 is



R^7 is



R⁸ and R¹³ are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R¹² and R¹⁷ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶ and R¹⁷ that are vicinal to one another, taken together may form a ring.

4. The process as recited in claim 3 wherein:

R¹, R² and R³ are hydrogen;

R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ is each independently halogen, alkyl containing 1 to 6 carbon atoms;

R⁸ and R¹³ is each independently hydrogen, halogen, or alkyl containing 1 to 6 carbon atoms;

R¹² and R¹⁷ is each independently halogen, hydrogen, or alkyl containing 1 to 6 carbon atoms; and R⁴ and R⁵ are each independently halogen, hydrogen or alkyl containing 1 to 6 carbon atoms.

5. The process as recited in claim 4 wherein R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵, and R¹⁶ are each hydrogen.

6. The process as recited in claim 5 wherein R⁸, R¹², R¹³, and R¹⁷ are each alkyl containing 1-6 carbon atoms.

7. The process as recited in claim 5 wherein R⁴ and R⁵ are each hydrogen or methyl.

8. The process as recited in claim 4 wherein:

R¹, R² and R³, R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are hydrogen, R⁴ and R⁵ are methyl, and R⁸, R¹², R¹³ and R¹⁷ are isopropyl;

R¹, R² and R³, R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are hydrogen, R⁴ and R⁵ are methyl, and R⁸, R¹², R¹³ and R¹⁷ are methyl;

R¹, R² and R³, R⁹, R¹⁰, R¹¹, R¹², R¹⁴, R¹⁵, R¹⁶ and R¹⁷ are hydrogen, R⁴ and R⁵ are methyl, and R⁸, and R¹³ are t-butyl; or

R¹, R² and R³, R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵, R¹⁶, R⁸, R¹², R¹³ and R¹⁷ are hydrogen, and R⁴ and R⁵ are methyl.

9. The process as recited in claim 1 wherein X is chloride, bromide or nitrate.

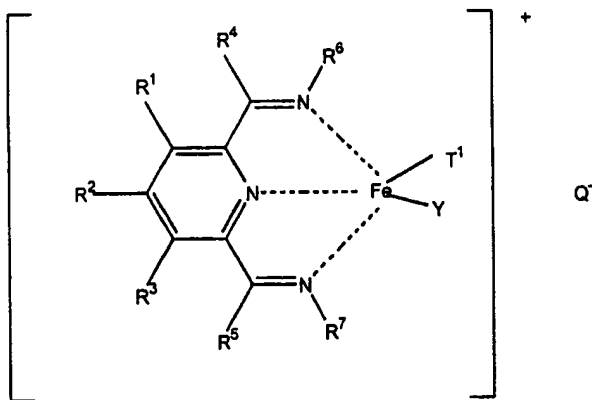
10. The process as recited in claim 4 wherein said neutral Lewis acid is an alkyl aluminum compound.

5 11. The process as recited in claim 10 wherein said alkyl aluminum compound is polymethylaluminoxane.

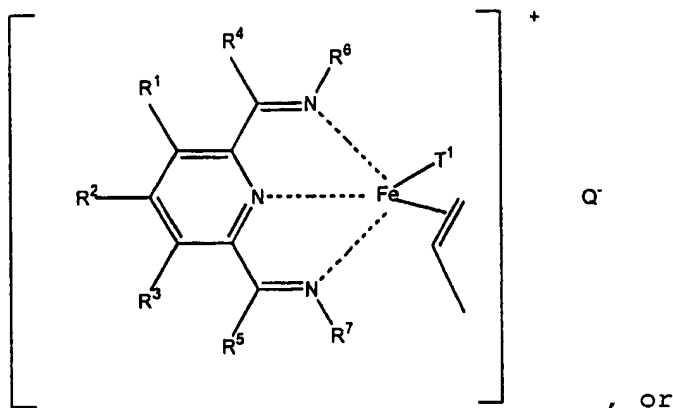
12. The process as recited in claim 4 wherein said temperature is about 0°C to about 100°C.

13. The process as recited in claim 1 wherein R²⁰
10 contains 1 to 4 carbon atoms.

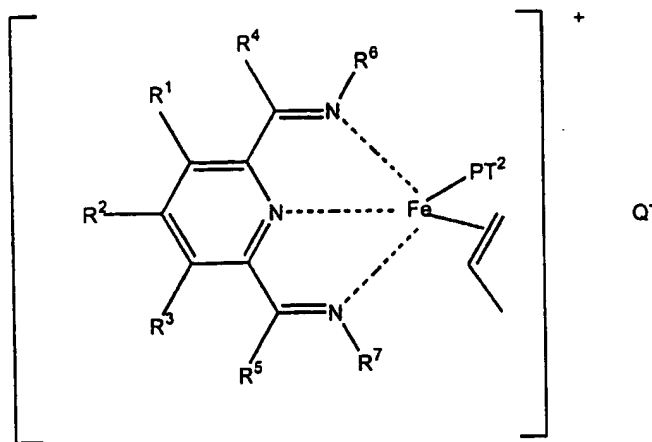
14. A process for the polymerization of propylene, comprising, contacting, at a temperature of about -40°C to about +300°C, propylene and a compound of the formula



(VII)



(XII)



(IX)

wherein:

5 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl;

10 R^6 and R^7 are aryl or substituted aryl;

T^1 is hydride or alkyl or any other anionic ligand into which propylene can insert;

Y is a neutral ligand capable of being displaced by propylene or a vacant coordination site;

15 Q is a relatively non-coordinating anion;

P is a divalent polyolefin group; and

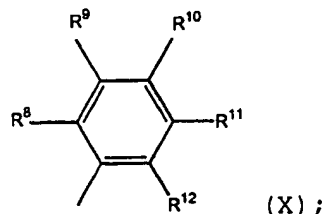
T^2 is an end group.

15. The process as recited in claim 14 wherein said compound is (VII).

20 16. The process as recited in claim 14 wherein said compound is (IX).

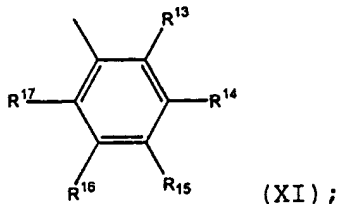
17. The process as recited in claim 14 wherein said compound is (XII).

25 18. The process as recited in claim 14 wherein: R^6 is



(X);

R⁷ is



R⁸ and R¹³ are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

5 R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R¹² and R¹⁷ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

10 and provided that any two of R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶ and R¹⁷ that are vicinal to one another, taken together may form a ring.

19. The process as recited in claim 18 wherein:

15 R¹, R² and R³ are hydrogen;

R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ is each independently halogen, alkyl containing 1 to 6 carbon atoms;

20 R⁸ and R¹³ is each independently hydrogen, halogen, or alkyl containing 1 to 6 carbon atoms;

R¹² and R¹⁷ is each independently halogen, hydrogen, or alkyl containing 1 to 6 carbon atoms; and

R⁴ and R⁵ are each independently halogen, hydrogen or alkyl containing 1 to 6 carbon atoms.

25 20. The process as recited in claim 19 wherein R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵, and R¹⁶ are each hydrogen.

21. The process as recited in claim 22 wherein R⁸, R¹², R¹³, and R¹⁷ are each alkyl containing 1-6 carbon atoms.

30 22. The process as recited in claim 20 wherein R⁴ and R⁵ are each hydrogen or methyl.

23. The process as recited in claim 17 wherein:

35 R¹, R² and R³, R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are hydrogen, R⁴ and R⁵ are methyl, and R⁸, R¹², R¹³ and R¹⁷ are isopropyl;

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are hydrogen, R^4 and R^5 are methyl, and R^8 , R^{12} , R^{13} and R^{17} are methyl;

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{12} , R^{14} , R^{15} , R^{16} and
5 R^{17} are hydrogen, R^4 and R^5 are methyl, and R^8 , and R^{13} are t-butyl; or

R^1 , R^2 and R^3 , R^9 , R^{10} , R^{11} , R^{14} , R^{15} , R^{16} , R^8 , R^{12} , R^{13} and R^{17} are hydrogen, and R^4 and R^5 are methyl.

24. The process as recited in claim 14, 15, 16 or
10 17 wherein said temperature is about 0°C to about 100°C.

25. The process as recited in claim 1 wherein said compound is or becomes part of a heterogeneous catalyst on a solid support.

15 26. The process as recited in claim 25 carried out in the gas phase or liquid phase.

27. The process as recited in claim 2 wherein said complex is or becomes part of a heterogeneous catalyst on a solid support.

20 28. The process as recited in claim 27 carried out in the gas or liquid phase.

29. The process as recited in claim 14 wherein (VI), (IX) or (XII) is part of a heterogeneous catalyst on a solid support.

25 30. The process as recited in claim 29 carried out in the gas or liquid phase.

31. The process as recited in claim 25, 27 or 29 wherein said solid support is silica or alumina.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US. 98/00316

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/06 C08F4/70

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 37523 A (BASF AG ;LIPPERT FERDINAND (DE); HOEHN ARTHUR (DE); SCHAUSS ECKARD) 28 November 1996 see abstract; page 4, line 13 to page 5, line 43; claims 1, 6 ---	1-31
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 270 (C-0727), 12 June 1990 & JP 02 078663 A (N O K SOGO GIJUTSU KENKYUSHO:KK), 19 March 1990, cited in the application see abstract --- -/--	1,31

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"8" document member of the same patent family

Date of the actual completion of the international search

19 May 1998

Date of mailing of the international search report

08/06/1998

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Mergoni, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/00316

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>NESPER R ET AL: "Palladium(II) complexes of chiral tridentate nitrogen pybox ligands"</p> <p>JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 1, no. 507, 25 January 1996, page 85-101 XP004036312</p> <p>see abstract; page 91, figure 211; page 92-93</p> <p>-----</p>	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/00316

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9637523 A	28-11-1996	EP 0827516 A	11-03-1998